

## Problem Set 5: Solutions

### Instructions:

1. Answer all questions below. Show your work for full credit.
2. All problems are due Thurs 7 March 2013 by the end of the day.
3. You may collaborate, but everyone must turn in their own work.

1. The state of a free particle is described by the following wave function

$$\psi(x) = \begin{cases} 0 & x < -b \\ A & -b \leq x \leq 7b \\ 0 & x > 7b \end{cases} \quad (1)$$

- (a) Determine the normalization constant  $A$ .
- (b) What is the probability of finding the particle in the interval  $[0, b]$ ?
- (c) Determine  $\langle x \rangle$  and  $\langle x^2 \rangle$  for this state.
- (d) Find the uncertainty in position  $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ .

**Solution:** (a) Normalizing means integrating the probability density over all space and setting the result equal to one. Since the wave function is only non-zero over the interval  $[-b, 7b]$ , we need not bother integrating over  $[-\infty, -b]$  or  $[7b, \infty]$ .

$$1 = \int |\psi|^2 dx = \int_{-b}^{7b} A^2 dx = A^2 x \Big|_{-b}^{7b} = 8bA^2 \quad (2)$$

$$\implies A^2 = \frac{1}{8b} \quad \text{or} \quad A = \frac{1}{2b\sqrt{2}} \quad (3)$$

- (b) The probability of finding the particle in  $[0, b]$  just means integrating the probability density over that interval.

$$P(x \in [0, b]) = \int_0^b |\psi|^2 dx = \int_0^b A^2 dx = A^2 x \Big|_0^b = bA^2 = \frac{1}{8} \quad (4)$$

This makes a lot of sense: the interval the wave function is confined over  $[-b, 7b]$  has width  $8b$ , and the odds of finding the particle in any particular slice of width  $b$  should just be  $1/8$  given the wave function is constant.

- (c) In order to find  $\langle x \rangle$  and  $\langle x^2 \rangle$ , we integrate  $xP(x)$  and  $x^2P(x)$  over all space, which again means over  $[-b, 7b]$  since  $\psi$  is zero elsewhere:

$$\langle x \rangle = \int_{-b}^{7b} x A^2 dx = A^2 \cdot \frac{1}{2} x^2 \Big|_{-b}^{7b} = \frac{1}{2} A^2 (49b^2 - b^2) = 24b^2 A^2 = 3b \quad (5)$$

$$\langle x^2 \rangle = \int_{-b}^{7b} x^2 A^2 dx = \frac{1}{3} A^2 x^3 \Big|_{-b}^{7b} = \frac{1}{3} \cdot \frac{1}{8b} \cdot (343b^3 + b^3) = \frac{43}{3} b^2 \quad (6)$$

Again, this is sensible: the particle is found, on average, in the center of the interval  $[-b, 7b]$  right at  $x=3b$ . Note that the standard deviation  $\langle x^2 \rangle$  is much larger than the interval itself ( $\sim 14b$  compared to  $8b$ ), so the particle is not well localized at all. In fact, once we calculate the uncertainty ...

(d) The uncertainty in position is found in the usual way:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{43}{3} b^2 - 9b^2} = b \sqrt{\frac{16}{3}} = \frac{4b}{\sqrt{3}} \approx 2.3b \quad (7)$$

If we were to measure the position of the particle, we would expect to get  $\langle x \rangle \pm \Delta x \approx 3b \pm 2.3b$  most of the time (68% of the time if the uncertainty is random). The bounds on  $\langle x \rangle$  are so large that all we can say with confidence is that the particle is somewhere within the region  $[-b, 7b]$ .

2. An electron in a helium atom is in a state described by the (normalized) wave function

$$\psi = \frac{4}{\sqrt{2\pi} (\alpha_0)^{3/2}} e^{-2r/\alpha_0} \quad (8)$$

where  $\alpha_0$  is the Bohr radius.

What is the *most probable* value of  $r$ ?

**Solution:** The most probable value of  $r$  would be the radius at which the probability distribution  $P(r)$  is maximum. Thus, we just need to find  $P(r)$ , calculate  $dP/dr$  and set it equal to zero, and we're done.

$$P(r) dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr \quad \text{or} \quad P(r) = 4\pi r^2 |\psi|^2 \quad (9)$$

$$P(r) = 4\pi r^2 \left( \frac{8}{\pi \alpha_0^3} e^{-4r/\alpha_0} \right) = \frac{32r^2}{\alpha_0^3} e^{-4r/\alpha_0} \quad (10)$$

Now the derivative:

$$\frac{dP}{dr} = \frac{32}{a_0^3} \left( 2re^{-4r/a_0} - \frac{4r^2}{a_0} e^{-4r/a_0} \right) = 0 \quad (11)$$

$$\implies 0 = 2r - \frac{4r^2}{a_0} \implies 4r^2 = 2ra_0 \implies r = \frac{1}{2}a_0 \quad (12)$$

$$(13)$$

A quick plot of  $P(r)$  verifies that this is a maximum rather than a minimum. We have ignored the trivial solutions of  $r=0$  and  $r \rightarrow \infty$ .

**3.** The wave function for the ground state of hydrogen ( $n=1$ ) is

$$\psi_1 = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad (14)$$

where  $a_0$  is the Bohr radius.

(a) What is the *most probable* value of  $r$  for the ground state?

(b) What is the total probability of finding the electron at a distance greater than this radius?

**Solution:** (a) Just like the last problem.

$$P(r) = 4\pi r^2 |\psi|^2 = \frac{4r^2}{a_0^3} e^{-2r/a_0} \quad (15)$$

$$\frac{dP}{dr} = \frac{4}{a_0^3} e^{-2r/a_0} \left( 2r - \frac{2r^2}{a_0} \right) \quad (16)$$

$$\implies r = a_0 \quad (17)$$

Again, a quick plot shows  $r = a_0$  is a maximum in the probability distribution, so  $a_0$  is the most probable radius. We have again ignored the trivial solutions of  $r=0$  and  $r \rightarrow \infty$ .

(b) The odds of the electron being at a distance larger than this is found by integrating  $P(r) dV$  from  $a_0$  outward to  $\infty$ .

$$P(r > a_0) = \int_{a_0}^{\infty} |\psi|^2 \cdot 4\pi r^2 dr = \int_{a_0}^{\infty} \frac{4r^2}{a_0^3} e^{-2r/a_0} dr \quad (18)$$

The substitution  $u = 2r/a_0$ ,  $du = 2 dr/a_0$  makes this into a known integral. The limits then become 2 and  $\infty$

$$P(r > a_0) = \int_{\frac{a_0}{2}}^{\infty} \frac{u^2}{a_0} e^{-u} \frac{a_0}{2} du = \frac{1}{2} \int_{\frac{a_0}{2}}^{\infty} u^2 e^{-u} du = \frac{1}{2} (-e^{-u}) (u^2 + 2u + 2) \Big|_{\frac{a_0}{2}}^{\infty} \quad (19)$$

$$= \frac{1}{2} e^{-2} (10) = \frac{5}{e^2} \approx 0.677 \quad (20)$$

The probability distribution is rather asymmetric - there is approximately a 2 in 3 chance of finding the particle farther from the nucleus than the most probable radius.

4. Schrödinger's equation for a simple harmonic oscillator reads

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \psi = E \psi \quad (21)$$

The ground state wave function has the form

$$\psi_0 = a e^{-\alpha^2 x^2} \quad (22)$$

Determine the value of the constant  $\alpha$  and the energy of the state.

**Solution:** Nothing to do but plug in  $\psi$  and grind through it. First we can normalize  $\psi$  since it is easy:

$$1 = \int_{-\infty}^{\infty} |\psi|^2 dx = a^2 \int_{-\infty}^{\infty} e^{-\alpha^2 x^2} dx = \frac{\sqrt{\pi}}{|\alpha|} a^2 \implies \alpha^2 = \pi a^4 \quad (23)$$

This doesn't help much, but we can at least relate  $\alpha$  and  $a$ . Next find the derivatives of  $\psi$ .

$$\frac{\partial \psi}{\partial x} = -2\alpha^2 x a e^{-\alpha^2 x^2} \quad (24)$$

$$\frac{\partial^2 \psi}{\partial x^2} = -2\alpha^2 a e^{-\alpha^2 x^2} + 4\alpha^4 x^2 a e^{-\alpha^2 x^2} \quad (25)$$

$$= a e^{-\alpha^2 x^2} (4\alpha^4 x^2 - 2\alpha^2) = (4\alpha^4 x^2 - 2\alpha^2) \psi \quad (26)$$

Now the Schrödinger equation:

$$E \psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \psi = -\frac{\hbar^2}{2m} (4\alpha^4 x^2 - 2\alpha^2) \psi + \frac{1}{2} m \omega^2 x^2 \psi \quad (27)$$

Now we notice that all terms have a factor  $\psi$ , which we can cancel out, and all terms have either a constant or an  $x^2$  in front of them. The  $x^2$  and constant terms can't equal one another, so we

separately equate them. First the constant terms:

$$\frac{\hbar^2 \alpha^2}{m} = E \quad (28)$$

Now the  $x^2$  terms:

$$\frac{2\alpha^4 \hbar^2}{m} = \frac{1}{2} m \omega^2 \quad (29)$$

$$\alpha^4 = \frac{1}{4} \frac{m^2 \omega^2}{\hbar^2} \quad (30)$$

Combining, we can put  $E$  and  $\alpha$  in terms of fundamental constants and  $\omega$ .

$$E = \frac{\hbar^2}{m} \sqrt{\frac{m^2 \omega^2}{4\hbar^2}} = \frac{\hbar m \omega}{2m} = \frac{1}{2} \hbar \omega \quad (31)$$

$$\alpha = \sqrt[4]{\frac{m^2 \omega^2}{4\hbar^2}} = \sqrt{\frac{m\omega}{2\hbar}} \quad (32)$$

$$a = \sqrt{\alpha \sqrt{\pi}} = \sqrt[4]{\frac{\pi m \omega}{2\hbar}} \quad (33)$$

5. A phenomenological expression for the potential energy of a bond as a function of spacing is given by

$$U(r) = \frac{A}{r^n} - \frac{B}{r^m} \quad (34)$$

For a stable bond,  $m < n$ . Show that the molecule will break up when the atoms are pulled apart to a distance

$$r_b = \left( \frac{n+1}{m+1} \right)^{1/(n-m)} r_o \quad (35)$$

where  $r_o$  is the equilibrium spacing between the atoms. Be sure to note your criteria for breaking used to derive the above result.

**Solution:** The potential  $U(r)$  has an associated force, the molecule's restoring force:

$$F(r) = -\frac{dU}{dr} \quad (36)$$

The molecule will break when its maximum restoring force is reached, when  $dF/dr = -d^2U/dr^2 = 0$ . Equilibrium is when  $F = -dU/dr = 0$ . At the equilibrium spacing  $r_o$ , the force is zero, or equivalently, the potential is at a minimum.

$$F(r_o) = -\left.\frac{dU}{dr}\right|_{r_o} = \frac{nA}{r_o^{n+1}} - \frac{mB}{r_o^{m+1}} = 0 \quad (37)$$

$$\frac{nA}{mB} = \frac{r_o^{n+1}}{r_o^{m+1}} = r_o^{n-m} \quad (38)$$

$$r_o = \left(\frac{nA}{mB}\right)^{\frac{1}{n-m}} \quad (39)$$

Is this really a minimum for  $U$ ? We can check with the second derivative test: if  $d^2U/dr^2 = -dF/dr > 0$  at  $r_o$ , have a maximum. We will need  $dF/dr$  shortly anyway. You didn't really need to do this on your homework, but it is instructive:

$$-\frac{dF}{dr} = \frac{d^2U}{dr^2} = \frac{n(n+1)A}{r^{n+2}} - \frac{m(m+1)B}{r^{m+2}} \quad (40)$$

$$\left.\frac{d^2U}{dr^2}\right|_{r_o} = n(n+1)A \left(\frac{mB}{nA}\right)^{\frac{n+2}{n-m}} - m(m+1)B \left(\frac{mB}{nA}\right)^{\frac{m+2}{n-m}} \quad (41)$$

$$= \left(\frac{mB}{nA}\right)^2 \left[ n(n+1)A \left(\frac{mB}{nA}\right)^{\frac{n}{n-m}} - m(m+1)B \left(\frac{mB}{nA}\right)^{\frac{m}{n-m}} \right] \quad (42)$$

$$= \left(\frac{mB}{nA}\right)^2 \left(\frac{mB}{nA}\right)^{\frac{n}{n-m}} \left[ n(n+1)A - m(m+1)B \left(\frac{mB}{nA}\right)^{\frac{m-n}{n-m}} \right] \quad (43)$$

$$= \left(\frac{mB}{nA}\right)^2 \left(\frac{mB}{nA}\right)^{\frac{n}{n-m}} \left[ n(n+1)A - m(m+1)B \left(\frac{nA}{mB}\right) \right] \quad (44)$$

$$= \left(\frac{mB}{nA}\right)^{\frac{n+2}{n-m}} \left[ n(n+1)A - n(m+1)A \right] \quad (45)$$

$$= nA \left(\frac{mB}{nA}\right)^{\frac{n+2}{n-m}} \left[ n - m \right] > 0 \quad (46)$$

Clearly, the only way this expression will be positive is if  $n > m$ , which means stable bonds have  $n > m$ . This means that the repulsive force has a higher index than the attractive force, and it is of shorter range.

What about breaking the molecule? For distances smaller than  $r_o$ , the force is repulsive, while for distances greater than  $r_o$  it is attractive – in either case, it serves to try and restore the equilibrium position. However, the competition between the shorter-range repulsive force and longer-range attractive force means that there is a critical distortion of the molecule for  $r > r_o$  at which the force is maximum, and any stronger force (or larger displacement) will separate the constituents to an arbitrarily large distance – the molecule will be broken.

We have the force between the molecular constituents above:

$$F(r) = \frac{nA}{r^{n+1}} - \frac{mB}{r^{m+1}} \quad (47)$$

so we can readily calculate the maximum force with which the bond may try to restore its equilibrium. The force above is the force with which the molecule will respond if we push or pull on it. The maximum force will occur when  $dF/dr=0$ , at a radius  $r_b$

$$\left. \frac{dF}{dr} \right|_{r_b} = \frac{n(n+1)A}{r_b^{n+2}} - \frac{m(m+1)B}{r_b^{m+2}} = 0 \quad (48)$$

$$\frac{n(n+1)A}{m(m+1)B} = \frac{r_b^{n+2}}{r_b^{m+2}} = r_b^{n-m} \quad (49)$$

$$r_b = \left( \frac{n(n+1)}{m(m+1)B} \right)^{\frac{1}{n-m}} = \left( \frac{nA}{mB} \right)^{\frac{1}{n-m}} \left( \frac{n+1}{m+1} \right)^{\frac{1}{n-m}} \quad (50)$$

Now, how do we know this is the *maximum* force, and not a minimum force? We grind through another derivative ... we must have  $d^2F/dr^2 > 0$  for a maximum:

$$\frac{d^2F}{dr^2} = \frac{n(n+1)(n+2)A}{r^{n+3}} - \frac{m(m+1)(m+2)B}{r^{m+3}} = r^{n+3} \left[ n(n+1)(n+2)A - \frac{m(m+1)(m+2)B}{r^{m-n}} \right]$$

$$\left. \frac{d^2F}{dr^2} \right|_{r_b} = r_b^{n+3} \left( \frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[ n(n+1)(n+2)A - m(m+1)(m+2)B r_b^{n-m} \left( \frac{n+1}{m+1} \right)^{\frac{n-m}{n-m}} \right]$$

$$= r_b^{n+3} \left( \frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[ n(n+1)(n+2)A - m(n+1)(m+2)B r_b^{n-m} \right] \quad (51)$$

$$= r_b^{n+3} \left( \frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[ n(n+1)(n+2)A - m(n+1)(m+2)B \left( \frac{nA}{mB} \right) \right] \quad (52)$$

$$= r_b^{n+3} \left( \frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[ n(n+1)(n+2)A - n(n+1)(m+2)A \right] \quad (53)$$

$$= An(n+1)r_b^{n+3} \left( \frac{n+1}{m+1} \right)^{\frac{n+3}{n-m}} \left[ n-m \right] > 0 \quad (54)$$

For the second to last line, we noted that  $r_b^{n-m} = nA/mB$ . Once again, if  $n > m$ , the second derivative is positive, and thus the force is maximum at  $r_b$ . Applying a force sufficiently strong to stretch the bond to a separation  $r_b$  will serve to break it. Incidentally, the maximum force required is

$$\begin{aligned}
F(r_b) &= \frac{nA}{r_o^{n+1}} \left( \frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} - \frac{mB}{r_o^{m+1}} \left( \frac{n+1}{m+1} \right)^{\frac{m+1}{m-n}} = \left( \frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left[ \frac{nA}{r_o^{n+1}} - \frac{mB}{r_o^{m+1}} \left( \frac{n+1}{m+1} \right) \right] \\
&= \left( \frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left[ nA \left( \frac{nA}{mB} \right)^{\frac{n+1}{m-n}} - mB \left( \frac{nA}{mB} \right)^{\frac{m+1}{m-n}} \left( \frac{n+1}{m+1} \right) \right] \tag{55}
\end{aligned}$$

$$= \left( \frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left( \frac{nA}{mB} \right)^{\frac{n+1}{m-n}} \left[ nA - nA \left( \frac{n+1}{m+1} \right) \right] \tag{56}$$

$$= nA \left( \frac{n+1}{m+1} \right)^{\frac{n+1}{m-n}} \left( \frac{nA}{mB} \right)^{\frac{n+1}{m-n}} \left( \frac{m-n}{m+1} \right) = \frac{nA}{r_b^{n+1}} \left( \frac{m-n}{m+1} \right) \tag{57}$$